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Calculations on Cu clusters: Structure and Electronic Properties

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Abstract: The structure and electronic properties of small copper clusters are studied using Equivalent Crystal Theory (ECT) and a parametrised LCAO method. The minimum energy structure is obtained using ECT with Monte Carlo techniques. The LCAO method is then used to study the electronic properties of the optimized clusters.

Keywords: Clusters, nanostructures, LCAO, simulation

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I. Introduction

During the past few years much experimental and theoretical progress has been made towards the understanding of the physical and chemical properties of several elemental, binary and compound clusters.[1,2]. Apai *et al.*[3] carried out experiments on carbon-supported Cu clusters based on extended X-ray absorption fine structure studies. Balerna *et al.*[4] and Montano *et al.*[5] have carried out similar experimental studies on Au and Ag clusters. The localised *d* electrons in noble metals play an important role in the electronic structure through hybridisation with the more extended valence *s* states which needs to be taken into account in a careful theoretical treatment of these materials. Numerous theoretical studies of the atomic and electronic structure of various elements[6–9] have been performed. Recently the *ab initio* molecular dynamics (MD) approach of Car and Parinello (CP)[10] has been a promising development. However, the CP method is computationally intensive and there are difficulties in handling noble metals like Cu with this method.

In this paper we use a semi-empirical method to study the structures of small copper clusters of sizes 10 through 23. The Equivalent Crystal Theory (ECT),[11,12] which has been successfully applied to calculate the total energies of metals and semiconductors, is used to calculate the binding energy of the cluster. A Monte-Carlo technique is used to find the minimum-energy structure. Having obtained the optimum structure we use the LCAO (linear combination of atomic orbitals) method, particularly the parametrisation scheme due to Harrison,[13] to calculate various electronic properties like the binding energy per atom, the HOMO LUMO gap and the density of states.

II. Theory

A. Equivalent Crystal Theory

The Equivalent Crystal Theory is already well documented.[11,12,14] In this method the total energy E of a solid containing a defect is computed as if each atom were in an equivalent crystal at an appropriate lattice constant which is different from the equilibrium lattice constant. This single crystal is equivalent to the defect solid in the sense that it has the same total energy. The energy of this equivalent crystal (and hence the energy of the solid with defect) can then be determined from the Universal Binding Energy Relation (UBER)[15] as

$$E = \Delta E\, E^*(a^*)$$

where ΔE is the cohesive energy of the elemental crystal, $E^*(a^*)$ is a universal energy relation (see Fig. 9 of Ref.12),

$$a^* = \left(\frac{r_{ws} - r_{wse}}{l}\right), \qquad = \left[\Delta E/(d^2E/dr_{ws}^2)_{r_u}\right]^{\frac{1}{3}}$$

and r_{ws} is the Wigner-Seitz radius of the equivalent crystal and r_{wse} is the equilibrium Wigner-Seitz radius. The universal dimensionless function $E^*(a^*)$ is very well approximated by the Rydberg function:

$$E^*(a^*) = -(1 + a^*)e^{-a^*}$$

For further details of the theory the reader is referred to the original papers of Smith and Banerjea[11,14] and Smith *et al.*[12]

B. LCAO theory

The LCAO method used in this paper is described by Harrison.[13] The electronic structure Hamiltonian can be constructed from the parameters $V_{ss\sigma}$, $V_{sd\sigma}$, $V_{sd\pi}$ etc. using the Slater-Koster scheme.[16] The d electron parameters for all transition metal systems can be found in Ref. 17 for use in tight binding methods. However, following Menon *et al.*,[18,19] we make use of Harrison's universal scheme[13] for the determination of the electronic tight binding parameters. Also these universal parameters have been found to be transferable.[13] The Hamiltonian parameters are determined from the dimensionless universal parameters $\eta_{ll'm}$ in terms of the interatomic distance d by the following prescription

$$V_{ll'm} = \eta_{ll'm}\frac{\hbar^2 r^{3/2}}{md^2}, \quad V_{ldm} = \eta_{ldm}\frac{\hbar^2 r^{3/2}}{md^{7/2}}, \quad V_{ddm} = \eta_{ddm}\frac{\hbar^2 r_d^3}{md^5}.$$

Here r_d is the d-state radius which for Cu has the value[13] 0.67Å. The parameters $\eta_{ll'm}$, η_{ldm} and η_{ddm} are also taken from the solid state table of Ref. 13 and have the values given by $\eta_{ss\sigma} = -1.40$, $\eta_{sd\sigma} = -3.16$, $\eta_{dd\sigma} = -16.20$, $\eta_{dd\pi} = 8.75$.

We have chosen a minimal basis set of five d states per atom and the s state. The diagonal matrix elements ϵ_s and ϵ_d of the Hamiltonian are simply the atomic term values given in Ref. 13. We set $\epsilon_s = \epsilon_d$ for reasons given in Refs. 13. and 18.

III. Computational Details

The structure optimisation was carried out using the ECT method which has been discussed in Section 2.1. We chose the starting configuration for our 13-atom cluster to be an icosahedron, since it is generally agreed that an approximately icosahedral structure has the minimum energy. We then added or deleted atoms from this structure to obtain the starting configurations for the other clusters. The details will be presented elsewhere.[20] The structure of each cluster was then relaxed to a local minimum by a zero-temperature Monte-Carlo method.

The binding energy per atom for the optimised clusters was calculated using the LCAO theory as follows. The total energy within a one particle treatment is given by

$$E_{tot} = \sum_{i,occ} \epsilon_i - E_{ee} + E_{II},$$

where ϵ_i are the eigenvalues of the single-particle Hamiltonian, E_{ee} refers to the total electron-electron interaction which includes Coulomb repulsion and exchange-correlation energy, and E_{II} denotes the Coulomb repulsion between the ions. We approximate the difference $E_{II} - E_{ee}$ in Eqn. (7) by a short ranged repulsive potential of the Born-Mayer (BM) type given as

$$E_{II} - E_{ee} \simeq E_{BM} = \frac{1}{2}{\sum_{i,j}}' A exp[-p(\frac{|R_i - R_j|}{d_b} - 1)]$$

Following Lammers and Borstel[21] we have used $A = 2.118 \times 10^{-2}$ Ry and $p = 14.7238$ for Cu.

IV. Results and Conclusions

We have obtained the binding energies of copper clusters for N = 10 through 23 using ECT as well as by the parametrised LCAO technique. Fig. 1 shows a comparison of the binding energy per atom for different cluster sizes obtained by the two methods. The dotted lines are the ECT results and the solid lines are from the LCAO calculations. We see from the figure that the values obtained by the two different methods agree quite well for cluster sizes 12 through 23. The agreement is particularly good for the range N = 14 through 20. Given the widely different approach to the energy calculation in the two different methods this agreement is quite remarkable. Significantly, the ECT values show a local minimum at cluster sizes 13, 19 and 21, while a corresponding minimum is not seen in the LCAO values. Between 13 and 19 the ECT values are slightly higher than the LCAO values. We believe the reason for this is that the cluster geometry was optimised with respect to the ECT calculations and not with respect to the LCAO calculations. The values for the binding energy per atom for Cu clusters given by Lammers *et al.*[21] are slightly larger in magnitude than our calculated values. On the other hand, Datta *et al.*[22] have reported binding energy values, calculated using the TB-LMTO formalism, which are slightly smaller in magnitude than our calculated values over the same range of cluster sizes.

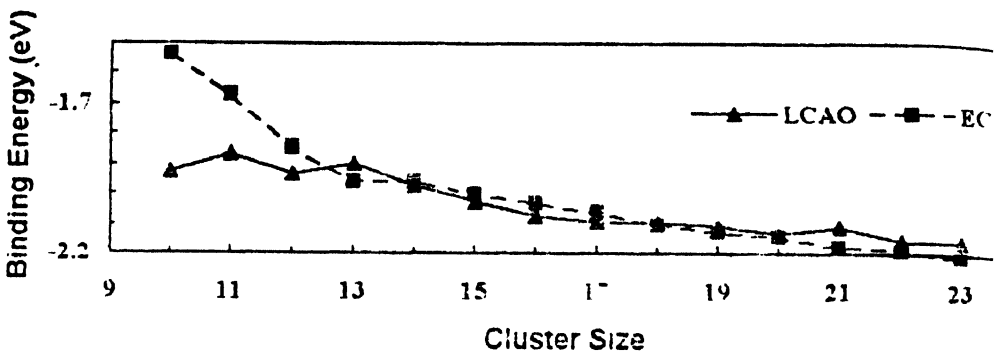

Fig. 1. Binding energy per atom from LCAO (solid line) and ECT (dotted line) plotted *vs.* cluster size.

Figure 2 shows the plot of HOMO-LUMO gap *versus* cluster size. The graph shows peaks at 13, 17, 20 and 23. The calculations of Lammers *et al.*[21] show the HOMO-LUMO gap to have peaks at 13, 20 and 23. However they find a minimum at N = 17. The values of the HOMO-LUMO gap from Ref. 21 are in general higher in magnitude than our values. Christensen *et al.*[24] have emphasized the structure dependence of the HOMO-LUMO gap. We attribute the differences between our HOMO-LUMO gap results and those of other authors to the difference in geometrical structures. Also we see no evidence of the pronounced odd-even alternation in the HOMO-LUMO gap values reported in Ref. 24. Such odd-even alternations were also not observed by Lammers *et al.*[21] in their TB-LMTO calculations.

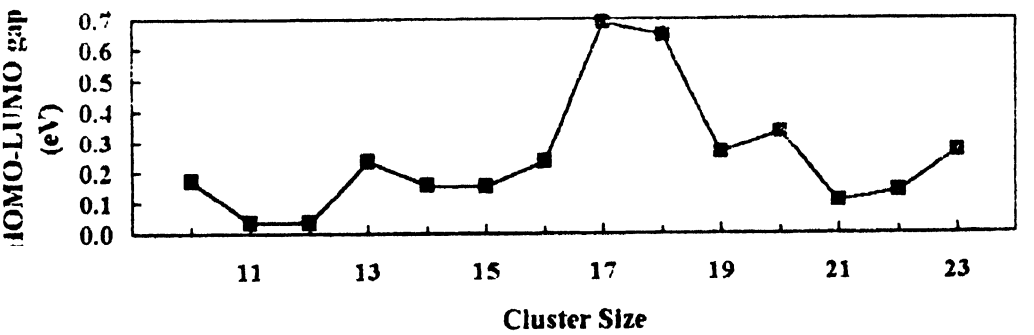

Fig. 2. Plot of HOMO-LUMO gap versus cluster size.

Figures 3 and 4 give the total pseudo-density of states (DOS) for clusters of sizes N = 10 and 20. The DOS plots were obtained by convoluting the energy levels of the clusters (as obtained from our LCAO calculations) with a Lorentzian of width .03 eV. The spin degeneracy has not been accounted for explicitly. Some features of the DOS plots deserve comment. The location of the broad peak is around -7 eV for all the cluster sizes. The lowest peak for Cu_{10} is around -16 eV while for Cu_{20} it is around -20 eV. So, as the cluster size increases the position of the lowest energy peak seems to move towards the lower energy side. There are peaks around -11 eV and -9.75 eV for Cu_{10} and for Cu_{20} there are two close peaks at -13.75 eV and -13.25 eV

and one peak at -12 eV. This movement of the peaks towards lower energy is observed in general as we move from N = 10 to 23. The height of the broad peak gets enhanced as we move from smaller clusters to larger clusters.

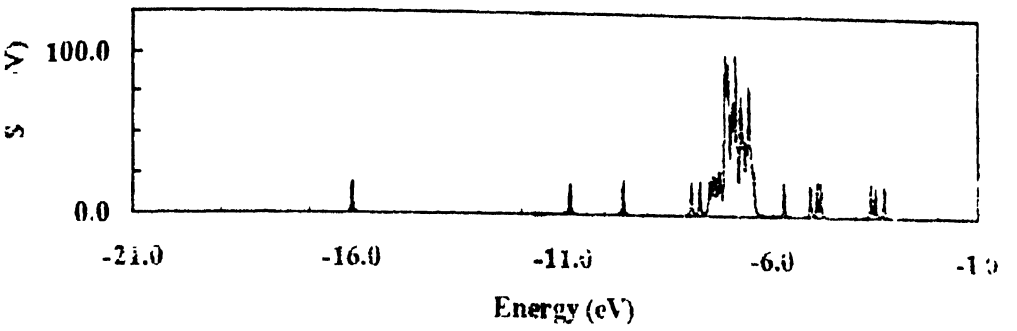

Fig. 3. Plot of total density of states for a 10-atom Copper cluster.

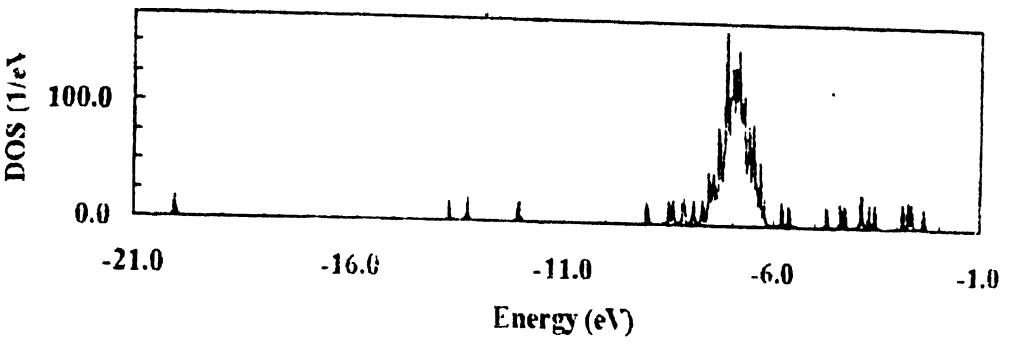

Fig. 4. Plot of total density of states for a 20-atom Copper cluster.

The binding energy per atom for small copper clusters using the ECT and the parametrised LCAO method are seen to be in good agreement over a wide range of cluster values, though these methods are widely different in principle. The HOMO-LUMO gap and DOS for copper clusters were calculated using the parametrised LCAO method. The computational resources required to perform the semi-empirical calculations in this paper are minimal compared to other computationally intensive *ab-initio* calculations. We conclude that semi-empirical methods can provide an interface between more accurate and time consuming *ab-initio* calculations and calculations which assume the form of the interatomic potentials.

Acknowledgements

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